

DECLARATION

I, Hideaki KOGURE, a subject of Japan residing at 3-7-9, Kudan-Minami, Chiyoda-ku, Tokyo 102-0074, Japan solemnly and sincerely declare:

That I have thorough knowledge of Japanese and English languages; and

That the attached pages contain a correct translation into English of the specification of the following Japanese Patent Application:

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October 30, 1997

I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false statements and the like so made, are punishable by fine or imprisonment, or both, under Section 1001, Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 6th day of June, 2005

Hideaki Kogure

Hideaki KOGURE

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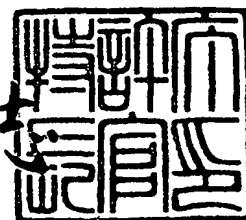
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[List of Documents Attached]

[Name of Document]	Specification	1
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[Name of Document] SPECIFICATION

[Title of the Invention] CARBON NANOTUBE DEVICE

[Claims]

[Claim 1] A carbon nanotube device which is a functional device using a carbon nanotube, wherein at least one terminus of said carbon nanotube binds to an electrode, and said binding site is isolated by a specific wall material.

[Claim 2] A carbon nanotube device according to claim 1, wherein said carbon nanotube is connected to the electrode via catalytic super-fine particles, and said catalytic super-fine particles comprise one or more metals selected from the group consisting of Fe, Co and Ni.

[Claim 3] A carbon nanotube device according to claim 1 or 2, wherein said wall material mainly comprises alumina.

[Claim 4] A carbon nanotube device according to claim 1 or 2, wherein said wall material mainly comprises silicon.

[Claim 5] A carbon nanotube device according to any one of claims 1 to 3, wherein said electrode is made of a material mainly comprising one or more metals selected from the group consisting of Ti, Zr, Nb, Ta, Mo, Cu and Zn.

[Claim 6] A carbon nanotube device according to any

one of claims 1 to 5, wherein connection of said catalytic super-fine particles and said electrode is a tunnel connection.

[Claim 7] A carbon nanotube device according to any one of claims 1 to 5, wherein electrons are emitted from the tip of said carbon nanotube by means of an electric field.

[Claim 8] A carbon nanotube device according to any one of claims 1 to 5, wherein an image is obtained by conducting scanning with the use of said carbon nanotube as a probe.

[Detailed Description of the Invention]

[0001]

[Industrial Field of the Invention]

The present invention relates to device using a carbon nanotube, and more particularly, to a carbon nanotube device effective as a functional device such as a quantum-effect device, an electronic device, a micro-machine device or a bio-device.

Further, the invention relates to a carbon nanotube device applicable to an electron source, an STM (scanning type tunnel microscope) probe, or an AFM (atomic force microscope) probe by the utilization of sharpness of the carbon nanotube.

[0002]

[Description of the Related Art]

Fibrous carbon is generally called carbon fiber, and for carbon fiber that is used as a structural material having a diameter of at least several μm , several manufacturing methods have been studied. Among those studied, a method for manufacturing the carbon fiber from a PAN (polyacrylonitrile)-based fiber or a pitch-based fiber is considered to be a mainstream method.

Schematically, this method comprises making a raw material spun from a PAN fiber, an isotropic pitch or a meso-phase pitch non-meltable and hardly flammable, carbonizing the resultant material at a temperature within a range of from 800 to 1,400°C, and treating the resultant product at a high temperature within a range of from 1,500 to 3,000°C. The carbon fiber thus obtained is excellent in mechanical properties such as strength and modulus of elasticity, and for its light weight that can be used for a sporting good, an adiabatic material and a structural material for space or automotive purposes in the form of a composite material.

[0003]

On the other hand, a carbon nanotube has recently been discovered having a tubular structure whose diameter is 1 μm or less. An ideal structure of the carbon nanotube is a tube formed with a sheet of carbon hexagonal

meshes arranged in parallel with its tube axis. A plurality of such tubes forms a nanotube. The carbon nanotube is expected to have characteristics like metals or semiconductors, depending upon both diameter of the carbon nanotube and the bonding form of the carbon hexagonal mesh sheet. Therefore, the carbon nanotube is expected to be a functional material in the future.

Generally, carbon nanotubes are synthesized by the

application of the arc discharge process, a laser evaporation process, a pyrolysis process and the use of plasma.

[0004]

An outline of a recently developed carbon nanotube will now be described.

(Carbon nanotube)

A material having a diameter of up to 1 μm , smaller than that of carbon fiber, is popularly known as a carbon nanotube to discriminate from carbon fiber, although there is no definite boundary between them. In the invention, a long and slender material having a diameter of at least several μm shall be referred to as a "carbon fiber", and a long and slender material having a diameter of up to 1 μm , as a "carbon nanotube".

[0005]

In a narrower sense of the words, a material having

the carbon hexagonal mesh sheet of carbon substantially in parallel with the axis is called a carbon nanotube, and one with amorphous carbon surrounding a carbon nanotube is also included within the category of carbon nanotube.

[0006]

The carbon nanotube in the narrower definition is further classified into one with a single hexagonal mesh tube is called a single-walled nanotube (abbreviated as "SWNT"), and one comprising a tube of a plurality of layers of hexagonal meshes is called a multi-walled nanotube (abbreviated as "MWNT").

Which of these types of carbon nanotube structures is available is determined to some extent by the method of synthesis and other conditions. It is however not as yet possible to produce carbon nanotube of the same structure.

[0007]

These structures of a carbon nanotube are briefly illustrated in Fig. 1. Of Figs. 1(a) to 1(d), the left side drawings are schematic transverse sectional views of a carbon nanotube and carbon fiber, and the right side drawings are schematic sectional views illustrating longitudinal sections thereof.

[0008]

The carbon fiber has a shape as shown in Fig. 1(a) in which the diameter is large and a cylindrical mesh

structure in parallel with its axis has not grown. In the gas-phase pyrolysis method using a catalyst, a tubular mesh structure is observed in parallel with the axis near the tube center as shown in Fig. 1(b), with carbon of irregular structures adhering to the surrounding portions in many cases.

[0009]

Application of the arc discharge process or the like gives an MWNT in which a tubular mesh structure in parallel with its axis grows at the center as shown in Fig. 1(c) with a slight amount of amorphous carbon adhering to surrounding portions. The arc discharge process and the laser deposition process tend to give an SWNT in which a tubular mesh structure grows as shown in Fig. 1(d).

[0010]

The following three processes are now popularly used for the manufacture of the aforementioned carbon nanotube: a process similar to the gas-phase growth process for carbon fiber, the arc discharge process and the laser evaporation process. Apart from these three processes, the plasma synthesizing process and the solid-phase reaction process are known.

[0011]

These three representative processes will now be

described:

(1) Pyrolysis process using catalyst

This process is substantially identical with the carbon fiber gas-phase growth process. The process is described in C. E. Snijders et al., International Patent No. W089/07163 (International publication Number). The disclosed process comprises the steps of introducing ethylene or propane with hydrogen into a reactor, and simultaneously introducing super fine metal particles.

Apart from these raw material gases, a saturated hydrocarbon such as methane, ethane, propane, butane, hexane, or cyclohexane, and an unsaturated hydrocarbon such as ethylene, propylene, benzene or toluene, acetone, methanol or carbon monoxide, containing oxygen, may be used as a raw material.

[0012]

The ratio of the raw material gas to hydrogen should preferably be within a range of from 1:20 to 20:1. A catalyst of Fe or a mixture of Fe and Mo, Cr, Ce or Mn is recommended, and a process of attaching such a catalyst onto fumed alumina is proposed.

The reactor should preferably be at a temperature within a range of from 550 to 850°C. The gas flow rate should preferably be 100 sccm per inch diameter for hydrogen, and about 200 sccm for the raw material gas containing carbon.

A carbon tube is generated in a period of time within a range of from 30 minutes to an hour after introduction of fine particles.

[0013]

The resultant carbon tube has a diameter of about 3.5 to 75 nm and a length of from 5 to even 1,000 times as long as the diameter. The carbon mesh structure is in parallel with the tube axis, with a slight amount of pyrolysis carbon adhering to the outside of the tube.

[0014]

H. Dai et al. (Chemical Physics Letters 260, 1996, p. 471-475) report that, although at a low generating efficiency an SWNT is generated by using Mo as a catalytic nucleus and carbon monoxide gas as a raw material gas, and causing a reaction at 1,200°C.

[0015]

(2) Arc discharge process

The arc discharge process was first discovered by Iijima, and details are described in the Nature (vol. 354, 1991, p. 56-58). The discharge process is a simple process of carrying out DC arc discharge by the use of carbon rod electrodes in an argon atmosphere at 100 Torr. A carbon nanotube grows with carbon fine particles of 5 to 20 nm on a part of the surface of the negative electrode. This carbon tube has a diameter of from 4 to 30 nm and a

length of about 1 μm , and has a layered structure in which 2 to 50 μm tubular carbon meshes are laminated. The carbon mesh structure is spirally formed in parallel with the axis.

The pitch of the spiral differs for each tube and for each layer in the tube, and the inter-layer distance in the case of a multi-layer tube is 0.34 nm, which substantially agrees with the inter-layer distance of graphite. The leading end of the tube is closed by a carbon network.

[0016]

T. W. Ebbesen et al. describe conditions for generating carbon nanotubes in a large quantity by the arc discharge process in the Nature (vol. 358, 1992, p. 220-222). A carbon rod having a diameter of 9 mm is used as a cathode and a carbon rod having a diameter of 6 mm, as an anode. These electrodes are provided opposite to each other with a distance of 1 mm in between in a chamber. An arc discharge of about 18 V and 100 A is produced in a helium atmosphere at about 500 Torr.

[0017]

At 500 Torr or under, the ratio of the carbon nanotubes is rather low, and at over 500 Torr, the quantity of generation decreases as a whole. At 500 Torr which is the optimum condition, the ratio of carbon nanotubes reaches over 75%.

The collection ratio of carbon nanotube is reduced also by causing a change in supplied power or changing the atmosphere to argon one. More nanotubes are present near the center of the carbon rod.

[0018]

(3) Laser evaporation process

The laser evaporation process was first reported by T. Guo et al. in Chemical Physics Letters (243, 1995, p. 49-54), and further, generation of a rope-shaped SWNT by the laser evaporation process is reported by A. Thess et al. in Science (vol. 273, 1996, 483-487).

[0019]

First, a carbon rod formed by dispersing Co or Ni is placed in a quartz tube, and after filling the quartz tube with Ar at 500 Torr, the entire combination is heated to about 1,200°C. Nd YAG laser is condensed from the upstream end of the quartz tube to heat and evaporate the carbon rod. Carbon nanotubes are thus accumulated in the downstream end of the quartz tube. This process is hopeful for selective preparation of SWNTs, and has a feature that SWNTs tend to gather to form a rope shape.

[0020]

The conventional art will now be described in terms of application of the carbon nanotube.

(Application of carbon nanotube)

While no applied product of carbon nanotube is available at present, active research efforts are being made for its applications. Typical examples of such efforts will be briefly described.

[0021]

(1) Electron emission source

The carbon nanotube, having a shape leading end and being electrically conductive, is adopted in many research subjects.

W. A. De Heer et al. refined a carbon nanotube obtained by the application of the arc discharge process, and placed it upright on a support via a filter to use it as a electron source (Science, vol. 270, 1995, p. 1179). They report that the electron source comprised a collection of carbon nanotube, and an emission current of at least 100 mA was stably obtained by the impression of 700 V from an area of 1 cm².

A. G. Rinzler et al. evaluated properties by attaching an electrode to a carbon nanotube obtained by the arc discharge process, and there was available an emission current of about 1 nA from a carbon nanotube with a closed end, and of about 0.5 μ A from a carbon nanotube with an open end, by the impression of about 75 V (Science, vol. 269, 1995, p. 1550).

[0022]

(2) STM, AFM

H. Dai et al. report, in Nature (384, 1996, p. 147), an application of a carbon nanotube to STM and AFM. According to their report, the carbon nanotube prepared by the arc discharge process was an SWNT having a diameter of about 5 nm at the leading end. Because of a thin tip and flexibility, even the bottom of a gap of a sample could be observed, and there was available an ideal tip free from a tip crash.

[0023]

(3) Hydrogen storing material

A. C. Dillon et al. report, in Nature (vol. 386, 1997, p. 377-379), that the use of an SWNT permits storage of hydrogen molecules of a quantity several times as large as that available with a carbon generated from a pitch-based raw material. While their study on application has just begun, it is expected to serve as a hydrogen storing material for a hydrogen car or the like.

[0024]

[Problems to be Solved by the Invention]

In the configuration and manufacturing method of a carbon nanotube in the conventional art, diameters and directions of resultant carbon nanotubes are very random, and after growth, an electrode is not connected to the carbon nanotube. More specifically, upon application of

the carbon nanotube, it is necessary to collect after synthesis for purifying, and form it into a particular shape in compliance with the shape for application.

[0025]

For example, when it is to be used as an election source, A. G. Rinzler et al. teaches the necessity to take out a carbon fiber and to bond an end thereof to an electrode, as reported in Science (vol. 269, 1995, p. 1550-1553).

Further, as reported in Science (vol. 270, 1995, p. 1179-1180) and Science (vol. 1, 268, 1995, p. 845-847), Walt A. de Heer et al. discloses the necessity to provide a step of purify a carbon nanotube prepared by the arc discharge process, and then placing upright the carbon nanotube on a support by the use of a ceramic filter. In this case, an electrode is not positively bonded to the carbon nanotube.

[0026]

Further, the carbon nanotube in application tend to get entangled with each other in a complicated manner, and it is difficult to obtain device fully utilizing characteristics of the individual carbon nanotubes. The present invention has an object to solve the above-mentioned problems.

[0027]

More specifically, the present invention has an object to provide a device in which an end of carbon nanotube is bonded to an electrode on a support to ensure efficient flow of current to the carbon nanotube, and another object to provide a device formed by separating individual carbon nanotubes from each other on the support.

Still another object of the invention is to provide a device in which the carbon nanotube is tunnel-bonded to the electrode, and further another object is to provide a device suitable for such uses as an electron source, an STM, and an AFM probes.

[0028]

[Means for Solving the Problems]

The aforementioned problems can be solved by the use of the device of the present invention and the manufacturing method thereof. The invention provides a carbon nanotube device using a carbon nanotube, wherein at least one terminus of the carbon nanotube binds to an electrode, and the binding site is isolated by a specific wall material.

[0029]

Catalytic super-fine particles are provided at the binding site of the electrode and the carbon nanotube for connection with the electrode via the fine particles. A

device provided with the catalytic super-fine particles comprising one or more metals selected from the group consisting of Fe, Co and Ni is preferable for growth control of the carbon nanotube. The wall material should preferably be made mainly of alumina or silicon in terms of insulation and heat resistance.

[0030]

Applicable materials mainly comprising silicon include silicon itself, silicon oxide and SiC. When the wall material is alumina, the electrode should preferably be made mainly of Ti, Zr, Nb, Ta, Mo, Cu or Zn for the preparation of porous alumina forming the wall.

[0031]

The catalytic super-fine particles and the electrode should preferably be connected by tunnel connection with a view to manufacturing a resonance tunnel device or the like. The device of the invention is particularly suitable for such applications as an electron source, an STM or an AFM probe.

[0032]

(Operation)

When manufacturing carbon nanotube by the pyrolysis process by simply seeding catalytic super-fine particles at a high density on a flat surface, there is a high probability that a carbon nanotube grows while causing

connection of many catalytic super-fine particles in and outside.

More specifically, directivity of a carbon nanotube connecting a plurality of catalytic super-fine particles as above is not uniform and the geometry including diameter cannot be linear. It is therefore desirable to cause individually isolated catalytic super-fine particles to grow.

While a carbon nanotube is often applied as an electrode, it is the general practice on the present level of art, after synthesis of the carbon nanotubes, to attach the carbon nanotubes to the substrate by conducting paste or scatter them onto the substrate and form a metal film on them.

[0033]

The carbon nanotube of the present invention is characterized by a configuration of the carbon nanotube in which, even without providing an electrode after synthesis, the carbon nanotube has a contact with the electrode by ohmic or tunnel junction. When manufacturing a device having such a configuration, the composition and the shape of the electrode, the catalytic super-fine particles, the wall separating the super-fine particles, and the method for synthesizing the carbon nanotube are important points.

[0034]

[Description of the Embodiments]

Embodiments of the present invention will now be described in detail.

First, the configuration will be described in detail with reference to Figs. 2 and 3.

In Fig. 2, 20 is a support; 21 is an undercoat electrode; 22 is a wall; 23 are catalytic super-fine particles; 24 is a carbon nanotube; and 25 is a semiconductor wall.

[0035]

Fig. 2(a) illustrates a case where an electrode layer is provided on the support, and catalytic super-fine particles thereon are surrounded by the wall. Fig. 2(b) show a case where the support serves also as an electrode. Fig. 2(c) is an example in which the wall and the electrode comprise semiconductor. Fig. 2(d) covers a case where the support, the electrode and the wall all comprise semiconductor.

In the aforementioned example, electrical junction between the carbon nanotube and the electrode may be in the form of an ohmic junction ensuring a sufficient connection, or of a shot-key junction. The junction property varies with the composition of the catalyst and the undercoat electrode layer and manufacturing conditions thereof.

[0036]

Fig. 3 represents an example in which the carbon nanotube and the electrode are connected in a tunnel junction. In Fig. 3, 30 is a support; 31 is an undercoat electrode layer; 32 is a wall for separating the carbon nanotube; 33 are catalytic super-fine particles; 34 is a carbon nanotube; and 35 is an insulating layer.

[0037]

In the example shown in Fig. 3(a), the undercoat electrode layer is provided on the support, with an insulating layer such as a surface oxide layer of the electrode thereon, and the catalytic super-fine particles separated by the wall is provided on the insulating layer, the carbon nanotube growing from the catalytic super-fine particles. In Fig. 3(b), the insulating layer is formed on the wall surface, and in Fig. 3(c), insulating layer is formed only on a portion where the wall is absent and the electrode layer surface is exposed. In Fig. 3(d), the support, the electrode and the wall are made of semiconductor, and the insulating layer is formed thereon. All these cases demonstrate a tunnel junction type connection, and the optimum thickness of the insulating layer, depending upon the composition and structure of the insulating layer, is substantially within a range of from sub-nm to several tens of nm.

[0038]

Figs. 2 and 3 illustrate only some typical examples of configuration, and the present invention is not limited to these configurations. For the manufacture of the wall, a general photolithographic method or an electron drawing method is applicable. In order to manufacture the wall further minutely and simply, the Al anode oxidation process or the Si anode chemical method is applicable.

[0039]

The Al anodic oxidation process is a process of oxidizing the surface of Al by using Al as an anode and Pt as a cathode in an oxalic acid solution, and impressing a voltage of about 40 V. In this process, narrow holes having a diameter of from several nm to several tens of nm are obtained on the Al surface, and the surface is simultaneously oxidized. In this case, the electrode can be exposed by forming the electrode layer with a material mainly comprising Ti, Zr, Nb, Ta, Mo, Cu or Zn under the Al film.

[0040]

It is also possible to prepare an insulating layer for tunnel by oxidizing the electrode surface upon exposure. In order to fill this narrow hole with the catalytic super-fine particles, the electro-deposition process is applicable. Si anode chemical process can be

carried out by flowing a current of several tens of mA/cm² in a fluoric acid solution with an Si substrate as an anode and platinum as cathode.

[0041]

For causing the carbon tube to grow on the site surrounded by the wall and on the support having the catalytic super-fine particles, it is effective to heat the support in a gas atmosphere comprising a raw material gas added with a diluent gas and a growth accelerating gas. Applicable raw material gases include many of gases containing carbon as described above.

[0042]

Examples of the raw material gas include gases comprising only carbon and hydrogen, such as methane, ethane, propane, butane, pentane, hexane, ethylene, acetylene, benzene, toluene and cyclohexane, and gases comprising carbon, hydrogen and other elements, such as benzonitrile, acetone, ethyl alcohol, methyl alcohol and carbon monoxide.

Preferable raw materials from among these applicable ones, somewhat varying with the kind of the support, the composition of the growth nucleus, growing temperature and pressure, are one comprising carbon, hydrogen and oxygen, which make it difficult for impurities to come in.

[0043]

In view of the low temperature growth of the carbon nanotube, ethylene, acetylene and carbon monoxide are preferable. Hydrogen is preferable as a growing or growth accelerating gas. However, because effectiveness of hydrogen depends upon the raw material gas, the reaction temperature, and the composition of the growth nucleus, hydrogen is not an essential requirement.

A diluent gas is effective when growth rate is too high, or when alleviating toxicity or explosivity of the raw material gas, and applicable diluent gases include inert gases such as argon and helium and nitrogen.

[0044]

An example of the manufacturing process of the carbon nanotube device thus obtained is illustrated in Fig. 5.

In Fig. 5, 50 is support; 51 is an undercoat electrode layer; 52 is a surface aluminum fiber; 53 is a narrow hole prepared by the anode oxidation alumina process; 54 are catalytic super-fine particles prepared by the electro-depositing process on the bottom of the narrow hole; and 55 is a carbon nanotube.

[0045]

The concept of the manufacturing method of the carbon nanotube device will be described with reference to Fig. 5.

First, as shown in Fig. 5(a), a film mainly comprising Ti,

Zr, Nb, Ta, Mo, Cu or Zn is formed on a support, and then and Al film is formed without exposure to the air. This film forming method is typically represented by the successive sputtering process based on a sputtering apparatus having multiple targets.

[0046]

Then, for anode oxidation, the support is immersed in a 0.3 M oxalic acid solution, and a voltage of 40 V is impressed while keeping a temperature of 17°C with the support as the anode and with Pt as the cathode. While impression of voltage first causes a rapid oxidation of the Al surface, leading to a decrease in the current value, later formation of the narrow hole results in an increase in current value to a constant level.

Upon completion of the Al film oxidation, the current value varies dependently upon the kind of the undercoat electrode layer. When completing the narrow hole piercing step by detecting this change in current value, a film having a narrow hole on the surface is obtained as shown in Fig. 5(b). When this narrow hole bore is to be expanded, it suffices to immerse the same in a phosphoric acid solution of about 5 wt.%.

[0047]

The AC electro-depositing process is effective for attaching the catalytic super-fine particular onto the

bottom of the narrow hole. When preparing a Co super-fine particle, for example, it suffices to impress an AC (50 Hz) voltage of about 15 V to a space between the conductive surface and the opposed electrode in an aqueous solution of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O} = 5\%$ and $\text{H}_3\text{BO}_3 = 2\%$.

[0048]

Growth of a carbon nanotube can be accomplished by the use of a reactor as shown in Fig. 4.

In Fig. 4, 41 is a reactor; 42 is a support; 43 is an infrared-ray absorbing plate, serving also as a support holder; 44 is a tube for introducing a raw material gas such as ethylene, and should preferably be arranged so as to achieve a uniform raw material gas concentration near the support; 45 is a tube for introducing a reaction accelerating gas such as hydrogen or a diluent gas such as helium; and the raw material tube is arranged near an infrared-ray transmitting window 49 so as to serve to prevent the window from being dim with decomposition of the raw material gas.

[0049]

Also in Fig. 4, 46 is a gas exhaust line which is connected to a turbo molecular pump or a rotary pump; 47 is an infrared lamp for heating the support; and 48 is a condensing mirror for collecting efficiently infrared rays for absorption. Although not shown, a vacuum gauge for

monitoring pressure within the container; a thermocouple for measuring temperature of the support and the like are provided.

[0050]

The apparatus is not of course limited to those described here. An electric furnace type apparatus heating the entire assembly from outside may well be employed. In actual growth of a carbon nanotube, steps comprise, for example, introducing ethylene as a raw material gas in an amount of 110 sccm from the raw material gas tube 44 into the apparatus, introducing 10 sccm hydrogen as the growth accelerating gas and diluent gas from the gas tube 45; applying a pressure of 1000 Pa in the reactor, heating the support by an infrared-ray lamp to 700°C and causing a reaction for 60 minutes.

[0051]

The thus synthesized carbon nanotube is shown in Fig. 5(d). The diameter of the carbon nanotube, depending upon the diameter of the catalytic super-fine particle and other reaction conditions, is within a range of from several nm to a submicron size and the length is within a range of from several tens of nm to several tens of μm . Since a terminus of the of the tube already binds to the substrate, the carbon nanotube device of the invention is favorable particularly in such applications as electric

field electron emission, a probe such as STM, a quantum device, a vibrator for a micromachine, and various electrodes.

Because carbon is chemically stable and has a high strength, the invention is applicable also for the purposes of improving the support surface.

[0052]

[Example]

The present invention will now be described in detail by means of sense examples with reference to the drawings.

[Example 1]

The carbon nanotube device of the invention and the manufacturing method thereof will be described by the use of the schematic process description view shown in Fig. 5 and the schematic view of the apparatus shown in Fig. 4. In Fig. 5, 50 is support; 51 is an undercoat electrode layer; 52 is a surface aluminum film; 53 is a narrow hole prepared by the anodic oxidation alumina process; 54 are catalytic super-fine particles prepared on the bottom of the narrow hole by the electro-deposition process; and 55 is a carbon nanotube.

[0053]

In Fig. 4, 41 is a reactor; 42 is a support; 43 is an infrared absorbing plate made of graphite, serving also as a support holder; 44 is a support; 43 is an infrared

absorbing plate made of graphite, serving also as a support holder; 44 is a tube for introducing a raw material gas, arranged so as to achieve a uniform raw material gas concentration in the proximity to the support; 45 is a tube for introducing hydrogen gas; and an infrared transmitting window 49 is arranged near the window so as to be useful for preventing clouding caused by decomposition of the raw material gas; 46 is a gas exhaust line, connected to a turbo molecular pump and a rotary pump; 47 is an infrared lamp for heating the support; and 48 is a condenser mirror for collecting infrared rays efficiently into the infrared absorbing plate.

In addition, a vacuum gauge for monitoring pressure in the vessel and a thermocouple for measuring in the vessel and of the support are incorporated. First, preparations of the support prior to causing growth of the carbon nanotube will be described.

[0054]

First, an electrode was prepared on the support. A cleaned Si wafer was used as a support, and a 100 nm-thick film was formed by the RF sputtering process from Ti, Zr, Nb, Ta, Mo, Cu, Zn, Pd or Au. The sputtering conditions included an RF power of 400 W and an AR atmosphere of 5 mTorr. Then, immediately an Al film of 1 μm was formed

under the same conditions, thereby preparing a support having the stacked structure as shown in Fig. 5(a).

[0055]

Subsequently, for anodic oxidation, the support was immersed in a 0.3 M oxalic acid solution, and voltage of 40 V was impressed, while keeping a temperature of 17°C, with the support as an anode and Pt as a cathode. Upon impression of the voltage, the Al surface was first rapidly oxidized, thus leading to a decrease in current value, and thereafter, along with emergence of the narrow hole, the current value increased to a constant level.

Upon completion of the oxidation of the Al film, the surface of the undercoat electrode layer was exposed. When the undercoat electrode layer comprised Ti, Zr, Nb, Ta, Mo, Cu or Zn, the current value rapidly decreased. The anodic oxidation was therefore discontinued at this point. This took a period of time of about ten minutes.

[0056]

To expand the bore of the narrow hole, the anode-oxidized support was immersed in a phosphoric acid solution of about 5 wt.% and then took it out, thus obtaining a film having a narrow hole of a diameter of about 50 nm on the surface thereof as shown in Fig. 5(b). In the case with an undercoat electrode layer of Pd or Au, the current value rapidly increased after the completion

of the anodic oxidation of Al and the narrow hole disappeared.

[0057]

Then, a catalytic super-fine particle was prepared by the AC electro-deposition process on the bottom of the narrow hole for. The support having narrow holes thus prepared was immersed in an aqueous solution containing 5% $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and 2% H_3BO_3 , and a structure having Co super-fine particles on the bottom of the narrow holes as shown in Fig. 5(c) was obtained by impressing an AC (50 Hz) voltage of 15 V for few seconds.

[0058]

Then, a carbon nanotube was grown in a reactor as shown in Fig. 4. First, the support having the catalytic super-fine particles was placed in the reactor, then hydrogen in an amount of 10 sccm was introduced from a gas tube 45 and a pressure of 500 Pa was kept in the reactor. The support temperature was brought to between 400 and 800°C by turning on an infrared lamp. After temperature stabilization, a raw material gas such as methane, ethylene, acetylene, carbon monoxide or benzene was introduced in an amount of 10 sccm from a raw material gas tube 44, and the pressure in the reactor of 1000 Pa kept for 20 minutes. Then, the infrared lamp was turned off to interrupt the supply of gas, and the support

was taken out into the open air after bringing the support temperature to the room temperature.

[0059]

The support thus taken out was observed by means of an FE-SEM (Field Emission-Scanning Electron Microscope). In all the observed supports, carbon nanotube had grown from the catalytic super-fine particles on the bottom of the narrow holes as shown in Fig. 5(d). The carbon nanotube had a diameter within a range of from several nm to several tens of nm, depending upon the raw material gas and the catalytic super-fine particle, and had grown in the vertical direction along the narrow hole from the support with a terminus of the carbon nanotube binding to the support.

[0060]

When methane was used as a source gas, however, growth of the carbon nanotube was less remarkable. With a source gas of benzene, there were fluctuations in diameter among carbon nanotube: the largest diameter was almost the same as that of the narrow hole. The optimum growth temperature of the carbon nanotube was higher in the order of carbon monoxide, acetylene, ethylene, benzene and then methane.

[0061]

For purpose of evaluating properties of the resultant

carbon nanotube devices, each carbon nanotube device was placed in a vacuum chamber, and an opposite electrode was arranged at a distance of 0.1 mm from the support in parallel therewith after attaching an electrode to the electrode film of the support. After evacuating the chamber to 10^{-8} Torr, a positive voltage was impressed to the opposite electrode, and the quantity of electrons emitted from the carbon nanotube was measured.

[0062]

As a result, as to the Group (1), (2) and (4) carbon nanotube devices, emitted current was observed when about 100 V of voltage was applied, and the amount of current when 200 V, was larger by a digit than that of the respective supports provided with the carbon nanotube coating.

This is attributable to the fact that the carbon nanotube were sufficiently connected to the electrode and the isolated carbon nanotubes extended in the vertical direction.

These results permitted confirmation that the device of the invention had an excellent function as an electron emitting source.

[0063]

[Example 2]

An example of the manufacturing method when the

catalytic metal and the electrode film are the same will now be described.

As in Example 1, by the use of an Si wafer substrate cleaned as a support, a Co film having a thickness of 0.1 μm was formed on the support by the RF simultaneous sputtering process. Then, in the same apparatus with the target changed to Al, and an Al film was continuously formed into a thickness of 0.2 μm to form an Al/Co layered film. The sputtering conditions included an RF power of 400 W and an Ar atmosphere at 5 mTorr.

[0064]

This support was immersed in a 0.3 M oxalic acid solution for anodic oxidation, and the Al film was anodically oxidized by using support as an anode and Pt as a cathode and impressing 40 V while keeping a temperature of 17°C. As a result of voltage impression, the Al surface was first rapidly oxidized, leading to a decrease in current value. After start of formation of narrow holes, the current value increased to a constant value. Upon the completion of oxidation of the Al film, the surface of undercoat Co layer appeared and the current value gradually increased. Anodic oxidation was therefore discontinued at this point. The period was for about two minutes.

[0065]

To widen the bore of the narrow holes, the support was immersed in a phosphoric acid solution of about 5 wt.% for 40 minutes and taken out, thus obtaining a film having narrow holes of a diameter of about 50 nm on the surface. As a result of this treatment, the undercoat Co surface was exposed on the bottom of the narrow holes and could be used as a catalyst portion.

[0066]

Then, the support was placed in a reactor as shown in Fig. 4, and hydrogen gas was introduced in an amount of 20 sccm from the growth accelerating gas tube 45 to bring the pressure in the reactor to 500 Pa. The support temperature was increased to 600°C by turning on an infrared lamp.

After stabilization of temperature, as a mixed raw material gas ethylene diluent with nitrogen to 10% was introduced in an amount of 20 sccm to bring pressure in the reactor to 1,000 Pa which was kept for 20 minutes. Thereafter, the infrared lamp was turned off to interrupt the supply of gas, and then, the support temperature was brought back to the room temperature. The support was then taken out into the open air.

[0067]

The surface of the resultant support was observed by means of an FE-SEM: carbon nanotubes had grown from the

narrow hole portion, but the carbon nanotubes had a large diameter of several 10 nm, and there were observed many portions of the narrow holes where the growth did not occur. This suggests that catalyst present in the narrow holes should preferably be in the form of super-fine particles as in Example 1.

[0068]

For the purpose of evaluating properties of the resultant carbon nanotube device, the electrode film of the support attached with an electrode was placed in a vacuum chamber as in Example 1, and an opposite electrode was arranged at a distance of 0.1 mm from the support in parallel therewith. After evacuating the chamber to 10^{-8} Torr, a positive voltage was impressed to the opposite electrode, and the quantity of electrons emitted from the carbon nanotubes was measured.

[0069]

As a result, emitted current was observed starting from impression of about 150 V, and the amount of current upon impressing 200 V, which was about a half that in Example 1, was several times as large as that available from a film in which carbon nanotube were simply dispersed.

This is considered attributable to the fact that, although the carbon nanotubes are sufficiently connected to the

electrode, the diameter of the nanotube is somewhat large, resulting in a low growth density of the carbon nanotube. This permitted confirmation that the device of the invention had a sufficient function as an electron emitting source.

[0070]

[Example 3]

An example of carbon nanotube device in which the super-fine particle wall, the electrode and the support are all prepared with Si will now be described with reference to the schematic process descriptive view shown in Fig. 6 and the equipment schematic diagram shown in Fig. 4.

[0071]

First, an ohmic contact was prepared by using a p-type substrate having a low resistance (several Ωcm to several hundred $\text{mm}\Omega\text{cm}$) as a support, forming an Al film having a thickness of about 1 μm on the back of the p-type Si to form narrow hole on the surface, and annealing at 400°C.

Then, anodization of the support was carried out with the support immersed in an aqueous solution containing 10% fluoric acid and 5% alcohol to serve as an anode and with Pt as a cathode. Al on the back was arranged so as not to come into contact with the fluoric acid solution, and an

electrode was taken from the Al surface. Conditions were set to give a current value of several tens of mA/cm² upon anodization. After the completion of anodization, the support was taken out, and washed with distilled water and IPA. As a result of this process, narrow holes of several nm to several tens of nm as shown in Fig. 6(a) were formed on the Si surface.

[0072]

The support was placed in a vacuum depositing unit and evacuation was carried out up to a degree of vacuum of 10⁻⁶ Torr, and Fe, Co Ni or Pd was vapor-deposited into a thickness of 0.3 nm on the upper surface by the resistance heating vapor depositing process. Thermal aggregation of the vapor-deposited film was accomplished by heating the support to 700°C while keeping a vacuum. This resulted in a structure in which catalytic super-fine particles 23 were placed in the narrow holes as shown in Fig. 6(b).

[0073]

Then, the support was placed in the reactor shown in Fig. 4. First, hydrogen gas was introduced in an amount of 20 sccm from the gas tube 45 to keep a pressure of 500 Pa in the reactor. The support temperature was increased to 650°C by turning on an infrared lamp. After stabilization of temperature, ethylene was introduced in an amount of 20 sccm to bring the pressure in the reactor

to 2,000 Pa, which was kept for 20 minutes. Thereafter, the infrared lamp was turned off to cut the supply of the gas. Then, after bringing the support temperature to the room temperature, the support was taken out into the open air.

[0074]

Observation of the resultant support surface by FS-SEM revealed that, while a carbon nanotube grew from the narrow hole site on the support having an Fe, Co or Ni film vapor-deposited thereon, almost no growth of a carbon nanotube was observed in the support having a vapor-deposited Pd film.

[0075]

For the purpose of evaluating properties of the resultant carbon nanotube devices, the electrode film of the support attached with an electrode was placed in a vacuum chamber, and an opposite electrode was arranged at a distance of 0.1 mm from the support in parallel therewith, as in Example 1. After evacuating the chamber to 10^{-8} Torr, a positive voltage was impressed to the opposite electrode, and the quantity of electrons emitted from the carbon nanotube was measured.

[0076]

As a result, the electron emission was observed from the impressed voltage, starting from impression of about

100 V, and the amount of current upon impressing 200 V was about ten times as large as that of a film in which carbon nanotubes were simply dispersed.

This is attributable to the fact that the carbon nanotubes were sufficiently connected to the electrode and the isolated carbon nanotubes extended in the vertical direction from the support.

This permitted confirmation that the device of the invention had an excellent function as an electron emitting source.

[0077]

[Example 4]

A configuration of tip type carbon nanotube device and a typical manufacturing method thereof will now be described with reference to the process schematic descriptive view shown in Fig. 7 and the equipment schematic diagram shown in Fig. 4.

[0078]

A resist 71 (AZ manufactured by Hext Company) was coated into a submicron thickness by means of a spinner as shown in Fig. 7(a) on a low-resistance Si wafer serving as a support 70. After UV exposure with the use of a mask, the exposed portion was peeled off with an organic solvent, and 0.1 to 1 μm (submicron) hole 72 was pierced on the resist. A hole 72 was prepared also in the Si

wafer by introducing the support into a plasma etching unit, and etching the Si wafer from the hole portion of the resist. The etching conditions included SF₄ gas of 5 Pa, an RF power of 150 W, and a treating period of a minute. Then, the support was placed in a resistance heating vapor depositing unit and a Co-Ni alloy (composing ratio: 1:1) film was formed into a thickness of 1 nm. Then, the resist was lifted off to remove an excessive portion, and thermal aggregation of the Co-Ni thin film was caused by annealing it in vacuum at 500°C to convert it into a catalytic super-fine particle 73 in Fig. 7(c).

[0079]

Then, the support was placed in the reactor shown in Fig. 4. First, hydrogen gas was introduced in an amount of 20 sccm from the gas growth accelerating/diluent gas tube 45 to keep a pressure of 500 Pa in the reactor. The support temperature was increased to 700°C by turning on an infrared lamp. After stabilization of temperature, acetylene gas diluted with 90% nitrogen was introduced in an amount of 20 sccm to bring the pressure in the reactor to 3,000 Pa, which was kept for 20 minutes. Thereafter, the infrared lamp was turned off to discontinue the supply of the gas. Then, after bringing the support temperature to the room temperature, the support was taken out into the open air.

The surface of the resultant support was observed with an FE-SEM. A carbon nanotube 74 had grown from the catalytic super-fine particle 73 portion in the hole 72 as shown in Fig. 7(d), having a diameter within a range of from several nm to several tens of nm.

[0080]

For the purpose of evaluating properties of the resultant carbon nanotube device, the support was attached to the probe portion of the STM/AFM evaluating unit to form a probe connected to an electrode. As a result of the STM/AFM evaluation, a satisfactory image based on a carbon nanotube tip was obtained.

This is considered to be due to a good directivity of the carbon nanotube surrounded by the wall, sufficient electrical connection between the carbon nanotube and the electrode (the low-resistance Si in this example), and the sharp tip thereof.

[0081]

[Example 5]

A typical configuration of a tunnel type carbon nanotube device will now be described with reference to the schematic diagram shown in Fig. 8.

[0082]

Electrodes 81 and 82 were prepared on a high-resistance or insulating support 80, and an aluminum

narrow hole film was horizontally formed adjacent to the electrode 81. A thin insulating layer was provided on a part of the electrode 82, and was connected to the carbon nanotube 84 thereabove via the insulating layer 87. An insulating coat film was provided over the insulating layer 87 and a wall 86.

A catalytic super-fine particle 85 was provided in the wall 86, and a carbon nanotube grew therefrom up to the electrode 82. The electrode 81 and the carbon nanotube were isolated from each other by the wall. The electrodes 81 and 82 were connected in the sequence of the electrode 81 - the wall insulating layer 86 - the catalytic super-fine particle 85, and the carbon nanotube 84 - the insulating layer 87 - the electrode 82.

[0083]

Current-voltage property of the resultant device having the aforementioned configuration was evaluated after connection of the electrodes by inserting it into liquid helium and cooling it to 4 K. A negative-resistance area was observed as a result in the current-voltage property. This is considered to be a result of a resonance tunnel effect because the device of the invention has double barriers. By the utilization of this phenomenon, the device of the invention is expected to be applied for high-frequency detection and

oscillation.

[0084]

[Advantages]

According to the carbon nanotube device of the present invention as described above, there are available the following remarkable advantages:

(1) There is available a satisfactory device electrically connected to electrodes and in which carbon nanotube are isolated from each other.

(2) An electron emitting device excellent in electron emitting property can be obtained.

(3) There is available a probe such as an STM or an AFM giving a satisfactory image and having a high strength.

(4) A novel tunnel type device using carbon nanotube is available.

[Brief Description of the Drawings]

[Fig. 1]

Schematic views illustrating various structures of a carbon nanotube: ((a) an isotropic carbon fiber; (b) a carbon nanotube with amorphous carbon therearound; (c) a multi-walled (carbon) nanotube; and (d) a single-walled (carbon) nanotube);

[Fig. 2]

Schematic views illustrating configurations of carbon

nanotube device: ((a) is an example of a configuration with different support, electrode and wall; (b) is a configuration in which a support and a electrode form a single body; (c) is a configuration in which an electrode and a wall form a single body; and (d) is a configuration in which a support, and electrode and a wall form a single body));

[Fig. 3]

Schematic conceptual views illustrating configurations of tunnel junction type carbon nanotube devices: ((a) is a configuration in which a support, an electrode, an insulating layer and a wall are different; (b) is a configuration in which an insulating layer is present on the surface of a wall; (c) is a configuration in which an insulating layer is present on a part of the surface of an electrode; and (d) is a configuration in which a support, an electrode, and a wall form a single body));

[Fig. 4]

A schematic view illustrating a carbon nanotube growing apparatus;

[Fig. 5]

A process diagram illustrating a manufacturing process of an upright type carbon nanotube device using alumina narrow holes:

((a) a sectional view of a support and an undercoat electrode and an Al film stacked thereon; (b) a sectional view of a surface Al layer provided with a narrow hole; (c) a sectional view of the narrow hole bottom with a catalytic super-fine particle electro-deposited thereon; and (d) a sectional view of the device after growth of the carbon nanotube);

[Fig. 6]

A schematic process diagram illustrating a manufacturing process of an upright type carbon nanotube device using Si narrow holes: ((a) a sectional view of an Si support provided with narrow holes; (b) a sectional view of the narrow hole with catalytic super-fine particles electro-deposited on the bottom thereof; and (c) a sectional view of the device after growth of the carbon nanotube);

[Fig. 7]

A schematic process diagram illustrating a manufacturing process of a tip type carbon nanotube device: ((a) a sectional view of a support coated with a resist thereon; (b) a sectional view of a support with narrow holes prepared thereon; (c) a sectional view of catalytic super-fine particles provided on the bottom of the narrow hole; and (d) a sectional view of the device after growth of the carbon nanotube); and

[Fig. 8]

A schematic process diagram illustrating a configuration of a tunnel type carbon nanotube device: ((a) a front view of the device; and (b) a sectional view of the device).

[Reference Numerals]

- 20, 30, 42, 50, 60, 70, 80 Support
- 21, 31, 51 Layer comprising a conductive surface
- 22, 32, 86 Wall
- 23, 33, 54, 62, 73, 85 Catalytic super-fine particle
- 24, 34, 55, 63, 74, 84 Carbon nanotube
- 25 Semiconductor wall
- 35, 87 Insulating layer
- 41 Reactor
- 43 Infrared-ray absorbing plate
- 44 Tube for introducing a raw material gas
- 45 Growth accelerating/diluent gas tube
- 46 Gas exhaust line
- 47 Infrared-ray lump
- 48 Infrared-ray Condensing mirror
- 49 Infrared-ray transmitting window
- 52 Al layer
- 53, 61 Narrow hole
- 71 Resist
- 72 Hole

81, 82 Electrode

83 Insulating coat film

[Name of Document] ABSTRACT

[Abstract]

[Object] The present invention has an object to provide a device ensuring efficient flow of current to a carbon nanotube by binding a terminus of the carbon nanotube to an electrode on a support, a device comprising individual carbon nanotube isolated from each other on a support; a device in which a carbon nanotube and an electrode are connected by tunnel junction, and a device suitable for application as an electronic source, or an STM or an AFM probe.

[Solving Means] The device of the invention is a functional one in which at least one terminus binds to an electrode and a binding site is isolated by a wall.

[Selected Figure] Fig. 8